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Review

Application of advanced oxidation processes for TNT removal: A review

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ABSTRACT

Nowadays, there are increasingly stringent regulations requiring drastic treatment of 2,4,6-trinitrotoluene (TNT) contaminated waters to generate treated waters which could be easily reused or released into the environment without any harmful effects. TNT is among the most highly suspected explosive compounds that interfere with groundwater system due to its high toxicity and low biodegradability. The present work is an overview of the literature on TNT removal from polluted waters and soils and, more particularly, its treatability by advanced oxidation processes (AOPs).

Among the remediation technologies, AOPs constitute a promising technology for the treatment of wastewaters containing non-easily biodegradable organic compounds. Data concerning the degradation of TNT reported during the period 1990–2009 are evaluated in this review. Among the AOPs, the following techniques are successively debated: processes based on hydrogen peroxide (H_2O_2 + UV, Fenton, photo-Fenton and Fenton-like processes), photocatalysis, processes based on ozone (O_3, O_3 + UV) and electrochemical processes. Kinetic constants related to TNT degradation and the different mechanistic degradation pathways are discussed. Possible future treatment strategies, such as, coupling AOP with biological treatment is also considered as a mean to improve TNT remediation efficiency and kinetic.

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1. Introduction

Over the last 150 years, globally millions of tonnes of nitroaromatic explosives have been produced for military applications and activities leading to accidental release of energetic materials to the environment causing soil and groundwater contamination [1]. Especially after World War I and II, great amounts of unsafe and out-of-date ammunition were left. The most widely used explosive for military applications is 2,4,6-trinitritoluene (TNT).

The US Army alone has estimated that over 1.2 million tons of soils have been contaminated with explosives, and the impact of such contamination in other countries is of similar magnitude [2]. The concentration of TNT in "hot spots" of contaminated soil can reach 50 g kg^{-1} soil [3], with the highest levels of TNT contamination directly located on or near the soil surface. In Canada, there were, in 2000, an estimated 103 training sites (air and land force bases) and three open burning/open detonation sites associated with activities involving TNT [4]. In Australia, some site characterization has been performed and also, in the rest of the world, the scope of the problem is significant [5]. For instance, countries that have suffered serious armed conflicts (e.g., recent wars in Africa, in the Middle East and in Eastern Europe) may be faced to similar problems, even though data on the extent of explosives contamination and the need to decontaminate polluted environments are not available. As a consequence, the United States Environmental Protection Agency (USEPA) established a remediation goal of 17.2 mg kg^{-1} of TNT in soils (the Nebraska Ordnance Plant) [6], a rigorous ambient criterion of 0.06 mg L^{-1} [7] and a drinking water criterion be lower than 0.01 mg L^{-1}. Recently, the U.S. Environmental Protection Agency has proposed a lifetime health advisory level of 2 μg L^{-1} for TNT in drinking water [8].

2. TNT

2.1. Structure and physicochemical properties of TNT

TNT is synthesized from toluene by a nitration process and consists of a benzene ring with nitro groups on positions 2,4,6 and a methyl group (Fig. 1). During its synthesis, undesired non-symmetrical isomers are removed by sulphite washing and the final product contains a few percent of impurities [9].

Both oxygen and nitrogen are two highly electronegative elements where oxygen possesses the highest electro negativity. The result is polarized N–O bonds within the nitro groups, which make them easily reducible [10]

Regarding the value of the octanol–water partition coefficient ($\log K_{OW} = 1.6$) given in Table 1, it can be concluded that the TNT molecule has an intermediate character between hydrophobic and hydrophilic properties, and that the TNT will not be sorbed strongly in soil/sediment and, therefore, may be relatively mobile in the environment. As TNT has very low vapour pressure, it can be considered as absent from the atmosphere. That is why, nitroaromatics associated with munitions have generally not been detected in atmospheric monitoring studies [11].

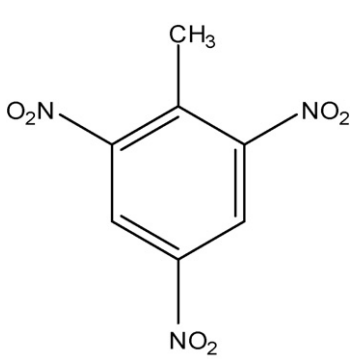

Fig. 1. 2,4,6-Trinitrotoluene.

Table 1
Physicochemical properties of TNT (adapted from Ek [104]).

CAS number	118-96-7
Chemical formula	$C_7H_5N_3O_6$
Molecular weight	227.13
Melting point	80.1 °C
Boiling point	240 °C
Water solubility at 20 °C	130 mg L^{-1}
Solubility in acetonitrile at 20 °C	100 g/100 g
Solubility in acetone at 20 °C	109 g/109
Vapour pressure	1.99×10^{-4} mm Hg
$\log K_{OW}$	1.6
$\log K_{OC}$	3.2
Henry's law constant (20 °C)	4.57×10^{-7} atm-m^3/mol

The mobility of TNT in groundwater or soil has been extrapolated from sorption and desorption isotherms models determined with humic acids, in aquifer sediments, and soils [12–15]. Sorption coefficients values obtained from these modelled systems have shown a pH dependency for sorption onto humic acids, but generally predict rather good transport (low retention) for TNT.

2.2. TNT: a toxic chemical compound

In addition to its worldwide distribution, the toxicity of TNT and its degradation products are extensively documented. The estimate of TNT risk is based on the determination of its toxicity or ecotoxicity and the potential for exposure. The toxicity of this compound has been widely studied in recent years using aquatic organisms terrestrial species such as earthworms, mammals or human monocytes (Table 2). The diversity of toxicity values obtained shows the diversity of sensitivity for different organisms tested. Toxic doses can also vary depending on exposure conditions and exposure times, but a reference dose for human exposure may be determined from these data. The health recommendation of the USEPA is 0.001 mg of TNT per liter of drinking water [16].

In conclusion, the problem with TNT-contaminated sites is its potential impact on ecosystem and living organisms (human, fauna and flora). Contact with humans can be done either directly by ingestion of water or indirectly by ingestion of plants grown on contaminated soil or that been irrigated by polluted water. Beyond the attacks on human health, polluted sites can disrupt certain soil functions: support to human activities, economic support to agricultural production or to support the biodiversity of terrestrial ecosystems. Furthermore, it is important to control such pollution because TNT can spread and reach the water surface by runoff, and groundwater by seepage. In the best of our knowledge, there is no specific law concerning TNT polluted sites and soils in the French legislation. However, regulations that can be applied to soil pollution from industrial sources specify the following three points: the general policy of rehabilitation of sites, the polluter pays principle and policy of risk assessment.

3. Physical and microbial processes for 2,4,6-trinitrotoluene degradation

Nowadays due to the increasing presence of TNT, refractory to the microorganisms in the wastewater streams, the conventional physical and biological processes cannot be used for complete TNT removal. However, a brief overview of some works on TNT removal using these kinds of processes is given here below.

Table 2
TNT acute and chronic toxicity.

Toxicity	Value	Exposure time	Organisms tested	TNT concentrations	References
No observed concentration time (NOEC)	0.48 mg L^{-1}	28 days	*Daphnia magna*	0.03–1.03 mg L^{-1}	[105]
	110 mg kg^{-1}	14 days	*Eisenia foetida*	0, 25, 50, 100 or 200 mg	[106]
	2.3 mg L^{-1}	48 h	*Brachinous calyciflorus*	-	[107]
Lowest observed concentration time (LOEC)	0.24 mg L^{-1}	28 days	*Daphnia magna*	0.03–1.03 mg L^{-1}	[105]
	150 mg kg^{-1}	14 days	*Eisenia foetida*	0, 25, 50, 100 or 200 mg	[106]
	5 mg L^{-1}	48 h	*Brachinous calyciflorus*	-	[107]
Lethal concentration (LC50)	1.5–29 mg L^{-1}	48 h	*Brachionus calyciflorus*, *Lumbricus variegatus*, *Daphnia magna*, and *Hyallela azteca* *Tanytarsus dissimilis Ictalurus punctatus*, *Lepomis macrochirus*, *Pimephales promelas* and *Oncorhynchus mykiss*		[108]
	0.46 mg L^{-1}	96 h	*L. macrochirus*		[109]
	325 mg kg^{-1}	14 days	*Eisenia foetida*	0, 25, 50, 100 or 200 mg	[106]

3.1. Physical processes for TNT removal

In the best of our knowledge, only few studies have been performed on the degradation of TNT by physical processes (i.e., sorption on activated carbon, catalytic sorption) in water. Indeed, Vasilyeva et al. [17] have investigated the TNT removal by activated carbon and further degradation. The analysis confirmed the presence of 2,4,6-trinitrobenzaldehyde (TNBAld) and 2,4,6-trinitrobenzene (TNB) and provided strong evidence supporting 2,4,6-trinitrobenzyl alcohol (TNBAlc) as an intermediate of TNT degradation. However, data regarding the removal kinetic and mineralization under this process has not been reported in this paper.

Saupe et al. [18] conducted lab-scale experiments on the alkaline hydrolysis of TNT and a mixture of TNT and soil followed by thermal treatment of the hydrolysates. Four hours of alkaline hydrolysis (T = 80 °C, initial pH 14) resulted in a complete deactivation of TNT and partial mineralization (90% of dissolved organic carbon (DOC) removal was achieved). Thus, the authors concluded that the alkaline hydrolyses of pure TNT was shown to be a safe deactivation process without detonation and with negligible gas production. The overall results suggest that alkaline hydrolysis followed by thermal and biological post treatment of the hydrolysates might be an efficient technology for the remediation of highly TNT-contaminated solution. But no by-products investigation was reported in the study of Saupe et al. [18]. Recently, Mills et al. [19] performed a kinetic study of the TNT removal rate under alkaline conditions and provided evidence that one of the molecules formed was a Meisenheimer complex.

In conclusion, the physical methods, such as cavitation, treatment with activated carbon, incineration techniques, alkaline hydrolysis and assisted soil washing with surfactants are very expensive and often require additional ex-situ treatment which may possibly produce new chemical by-products or waste gas emissions.

3.2. Microbial degradation of TNT

By definition, bioremediation is the use of living organisms, primarily microorganisms, to degrade the environmental contaminants into less toxic forms. It uses naturally occurring bacteria and fungi or plants to degrade or detoxify substances hazardous to human health and/or the environment. The microorganisms may be indigenous to a contaminated area or they may be isolated from elsewhere and brought to the contaminated site. Contaminant compounds are transformed by living organisms through reactions that take place as a part of their metabolic processes. Biodegradation of a compound is often a result of the actions of multiple organisms [20].

The bioremediation of explosives has been studied mainly with the objective of discovering microorganisms that may be inoculated in bio-reactor or directly *in situ* (bioaugmentation) in order to degrade the pollutant. Thus, many isolated microbial strains able to degrade or mineralize TNT have been identified from contaminated soils and waters [21]. Technologies based on biological processes have been developed for remediation of soils and waters contaminated by explosives. The main processes developed are bio-reactors seed with sludge, composting and "land farming" [10,22]. All these technologies require an ex-situ treatment, which means that the soil should be excavated. In all cases, intensive monitoring and a final evaluation of the remaining pollution are needed for taking into account the protection of the environment [23]. These treatments are adapted to highly explosives contaminated and hot spots. They are ill-suited to low and diffuse pollution.

In most of the described case, aerobic bacteria tend to transform the TNT molecule by reducing one or two nitro groups to hydroxylamino or amino groups and generate different isomers of amino nitroaromatic compounds, which in turn usually accumulate in the culture medium without further degradation. It has also been reported that partially reduced forms of TNT react between themselves, in the presence of oxygen, to form azoxytetranitrotoluene [24], which causes a higher rate of mutations than does the TNT itself. These transformation reactions remove TNT by yielding highly recalcitrant by-products that are not metabolizable by most of the microorganisms that produce them [25]. The aerobic bacteria are able to reduce two of the three NO_2 groups but reducing the third group requires anaerobic conditions. Anaerobic processes have the potential advantages of a rapid reduction at low redox potential, which minimizes oxidative polymerisation of substrates because of the absence of oxygen. This kind of TNT transformation results in the accumulation of triaminotoluene (TAT), but it is not sufficiently effective for bioremediation of contaminated sites [22].

Based on all these points, the TNT remediation of waters and soils is more than necessary. Consequently scientists and industrial companies are trying to find appropriate and effective processes for TNT removal. Therefore, there is a need to develop an effective advanced oxidation process (AOP) method based on the $OH^{\bullet}$ production for the degradation of these pollutants leading either to less harmful biodegradable compounds or to their complete mineralization. This review therefore focuses on the evaluation of advanced oxidation processes used for the TNT degradation and compare their TNT removal efficiency. This paper discusses the advantages and disadvantages of these processes and suggests some strategies to improve the effectiveness of these treatments.

4. Advanced oxidation processes (AOPs) as potential methods for TNT removal from contaminated environment

The treatment with advanced oxidation processes appears as one of the most promising methods for the treatment of soils and waters contaminated by nitroaromatic compounds and particularly TNT. Most of these processes have been associated with the generation of radical species mainly hydroxyl radicals ($OH^{\bullet}$). Hydroxyl radical is a strong oxidizing agent (E° = 2.8 vs. ENH at pH 0) able to react with organics and causing the ring opening. Unlike many other radicals, hydroxyl radicals is non-selective and thus readily attacks a large group of organic chemicals to convert them to less complex and less harmful intermediate products. At sufficient contact time and proper operation conditions, it is practically possible to mineralize the target pollutant to CO_2, which is the most stable end-product of chemical oxidation. The advantage of AOPs overall chemical and biological processes is that they are totally "environmental-friendly" as they neither transfer pollutants from phase to the other (as in chemical precipitation, adsorption, and volatilization) nor produce massive amounts of hazardous sludge [26]. The common AOPs developed for water and wastewater remediation and used for TNT removal are presented in Table 3. Some of these processes such as photolysis with more than 3000 applications in Europe as a disinfection process and a large number in the US for treating groundwater pollutants are commercially available [27].

Other processes such as combinations of H_2O_2, O_3, and UV, Fenton's reagent, and ionizing radiation have all been used for full scale applications. It should be noted that applications of AOPs in dual or triple combinations of individual processes offer significant kinetics and performance advantages. Methods of AOP employed in studying the degradability of TNT in water are displayed in Table 3.

4.1. Degradation of TNT by advanced oxidation processes

4.1.1. Overview of the Fenton chemistry

The oxidation processes based on the Fenton's reagent (hydrogen peroxide in the presence of a ferrous salt) have been used for the treatment of both organic and inorganic substances under laboratory conditions as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning, etc. [28]. The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants present in wastewater streams but the nature of these species is still under discussion and its formulation is a subject of controversy in the past and recent Fenton oxidation related literature [29–32].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}, \quad pH3, \quad k_1 = 70\,M^{-1}\,s^{-1} \quad (1)$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-}, \quad k_2 = 3.2 \times 10^{8}\,M^{-1}\,s^{-1} \quad (2)$$

$$Fe^{3+} + H_2O_2 \leftrightarrows Fe\text{-}OOH^{2+} + H^{+}, \quad k_3 = 0.001\text{–}0.1\,M^{-1} \quad (3)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2, \quad k_4 = 1.3 \times 10^{6}\,M^{-1}\,s^{-1}\,atpH3 \quad (4)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+}, \quad k_5 = 1.2 \times 10^{6}\,M^{-1}\,s^{-1}\,atpH3 \quad (5)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O, \quad k_6 = 3.3 \times 10^{7}\,M^{-1}\,s^{-1} \quad (6)$$

In the literature, three main reactive radical species have been observed. Two of them involve the presence of hydroxyl radicals (classical Fenton's chemistry) in either a 'free' or 'caged' form [33] whereas the third oxidant has been postulated to be aquo or organocomplexes of the high valence iron, the ferryl ion [34]. The rate of this reaction is strongly dependent on the presence of radical scavengers. It should be noted at this stage that both hydroxyl as well as ferryl complexes coexist in Fenton's mechanism and depending on the operating conditions (substrate nature, metal–peroxide ratio, scavengers addition, etc.), one of them will predominate. Nevertheless, the system can be most suitably applicable to discoloration and or removal of odor ingredients with good energy efficiency. Also, the oxidation system can be effectively used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for a secondary biological treatment [35]. Venkatadri and Peters [36], Bigda [37,28] and Nesheiwat and Swanson [38] have written good informative papers on the basics of Fenton chemistry as well as its application to wastewater treatment.

4.1.2. Fenton process

Chen et al. [39] investigated the TNT mineralization of spent acid produced from toluene nitration process by Fenton oxidation, by studying firstly the effects of given additions of ferrous ions, hydrogen peroxide and temperature on the mineralization of 0.65 mM mixture of nitroaromatic compounds in solution spent acid. These authors concluded then, that the optimal conditions of $[Fe^{2+}]$, $[H_2O_2]$ and temperature are 0.06 M, 7.6 M and 343 K, respectively; but they did not gave details regarding the degradation mechanism under such Fenton system, and their study was focused on a classical mineralization pathway under UV/Fenton.

Table 3
Main AOPs applied for TNT removal.

Advanced oxidation processes	Environment contaminated	References
Fenton	Ultrapure water	[39,40,110]
	Aqueous soil solution	[51,52]
Fe^0 coupled to Fenton	Aqueous soil solution	[111]
	Ultrapure water	[112,113]
	Industrial TNT wastewater	[120]
Fenton like	Ultrapure water	[93,114]
	Aqueous soil solution	[42,115]
UV/Fenton	Ultrapure water	[38,47,49]
	Aqueous soil solution	[46,50]
UV/H_2O_2	Ultrapure water	[39,45]
Photocatalysis with TiO_2	Ultrapure water	[67,68,116,117]
Photocatalysis with TiO_2 in presence of H_2O_2	Ultrapure water	[66]
Photocatalysis by porphyrins	Ultrapure water	[43]
O_3/H_2O_2	Ultrapure water	[44]
UV/O_3	Spent acid	[71]
Ultrasonic irradiation	Ultrapure water	[75]
Electrochemical reduction	Ultrapure water	[76,77,118]
Electro-Fenton	Ultrapure water	[89,90,100]

However, Fenton's oxidation was not, to the best of our knowledge, the subject of detailed TNT degradation mechanistic studies; this is why Ayoub et al. [40] were interested to: (i) study the influence of some parameters (i.e., Fe, H_2O_2) on TNT removal efficiency in the water by Fenton oxidation; (ii) determine apparent and absolute constant rates during TNT oxidation. They concluded that a ratio of $[H_2O_2]/[Fe^{2+}] = 10$ is required to obtain a rapid total TNT removal, (i.e., more than 98% removal rate was obtained using 0.5 mM, 2 mM and 20 mM of TNT, Fe(II) and H_2O_2, respectively). It should be noted that the ratio $[H_2O_2]/[Fe^{2+}]$ found in previous studies was also reported in the literature by other researchers during the treatment of phenols contaminated waters by Fenton process [41]. In contrast to what was previously showed in the literature, when Ayoub et al. [40] used a low $[H_2O_2]/[Fe^{2+}]$ molar ratio equal to 0.5 in presence of 1.25 mM Fe(II) and 0.625 mM H_2O_2, the TNT disappearance occurred in less than 30 min.

Matta et al. [42] studied Fenton-like oxidation of 0.11 mM TNT using different iron minerals (ferrihydrite, hematite, goethite, lepidocrocite, magnetite and pyrite) in aqueous solution. Fenton's reagent ($[H_2O_2] = 80$ mM, [Fe(II)] = 1.55 mM and pH 3.0) was able to degrade TNT in solution ($k_{app} = 0.0348\ min^{-1}$). When using iron oxide as heterogeneous catalyst at pH 3 ($[H_2O_2] = 80$ mM, [iron mineral] = 1.76 g L^{-1}), reaction rate constants were $k_{app} = 0.0055\ min^{-1}$ and $k_{app} = 0.2535\ min^{-1}$ for magnetite and pyrite, respectively, while ferric iron minerals were inefficient for TNT degradation. Matta et al. [42] showed that, when using pyrite as heterogeneous catalyst at pH 3, a rapid TNT abatement was registered but no TOC removal was recorded.

As a conclusion, it should be noted at this stage that both hydroxyl radicals as wall as iron (II) complexes coexist in Fenton's mechanism and depending fundamentally on the operating conditions (substrate nature, metal-peroxide ratio, scavengers addition, etc.), one of them will predominate. Exhaustive analyses of existing literature on application of Fenton oxidation was performed and indicates that the optimum condition for, pre-treated with zero-valent iron, TNT (0.24 mM) removal can be resumed to: 100% TOC and 92.2% N recovery by using a ratio $[H_2O_2]/[Fe^{2+}] = 5$ ($H_2O_2 = 25$ mM and $Fe^{2+} = 5$ mM at pH 3) within 2 h reaction times [112].

4.1.3. Direct and indirect photolysis with UV

UV photolysis has been one of the most widely investigated advanced oxidation method for TNT degradation based on the facts that UV irradiation is a common practice in drinking water process and photolysis is the main abiotic degradation pathway of organic matter in natural waters [43–45].

The following section is an overview and evaluation of such research carried out for TNT removal. Hwang et al. [45] employed UV/H_2O_2 advanced oxidation for the treatment of colored wastewater produced from alkaline hydrolysis of TNT-contaminated water. The effects of pH, and H_2O_2 dosage on the TNT removal were investigated and the authors showed that this treatment is able to decolorize the colored wastewater at the pHs studied (11.9, 6.5 and 2.5) within an reasonable treatment duration (i.e., less than 1 h). Enhanced decolorization was achieved with the increase in the H_2O_2 concentration and the decreased in the pH. Efficient decolorization and use of H_2O_2 were observed at pH 6.5 conditions. At pH 11.9, less decolorization was observed due to the scavenging properties of $OH^{\bullet}$ by CO_3^{2-}. Furthermore, when UV oxidation was coupled with 10 mg L^{-1} of $[H_2O_2]$ a 40% reduction of total organic carbon (TOC) concentration and 80% reduction in color intensity were indicated after 0.5-h reaction time.

Li et al. [46] studied the oxidation of 0.31 mM TNT by some processes (UV/Fenton at pH 3; UV + 0.15 M H_2O_2 at pH 3; UV only at pH 3; Fenton reagent in the dark at pH 3; 0.15 M H_2O_2 in the dark at pH 3; no Fenton at pH 3 and UV/Fenton at unadjusted pH). Li et al. [46] concluded that the oxidation efficiency decrease in the following order: UV/Fenton > Fenton reagent in the dark at pH 3 > UV/Fenton at unadjusted pH (6.1) > UV + 0.15 M H_2O_2 > UV only (dark). The TNT apparent rate constants were 0.017 min^{-1}, 0.031 min^{-1}, 0.04 min^{-1} for UV/Fenton at unadjusted pH, dark Fenton and UV/Fenton, respectively. For both dark and UV-mediated Fenton treatments, complete TNT soil extract solution transformation was observed, and total TNT destruction by UV/Fenton was achieved within 1 h and more than 95% mineralization was realized, compared to 45% of mineralization rate and 8 h in dark-Fenton treatment.

Liou et al. [47] investigated the photo-Fenton reaction (pH 2.8) for 50 min, the remaining TNT concentrations in solution, using 0.36 mM and 1.44 mM of Fe(II) with 0.29 M H_2O_2 were 48.4% and 5.9%, respectively. The degradation reaction rate of TNT followed a pseudo-first-order behaviour and the rate constants were 0.0135 min^{-1} and 0.0588 min^{-1}, respectively. This study was focused on the ways of improving the rate of TNT degradation and the possibility of using solar technologies in order to reduce operating costs by minimizing the energy consumption. Then, the oxidation rates significantly increased with increasing the concentration of Fe (II), as well as with the illumination with UV light. The TNT oxidation rate increased from 0.0588 min^{-1} to 0.0918 min^{-1}, respectively for the Fenton and photo-Fenton processes when the Fe (II) concentration was increased to 1.44 mM. Liou et al. [47] concluded that in photo-Fenton systems, ferrous ion and ultraviolet light significantly affected: (i) the efficiency of TNT degradation: in fact, applying ultraviolet light induces the reduction of ferric ions and photolysis of hydrogen peroxide to decompose TNT [48]; (ii) the pseudo-first-order constant for TNT oxidation (k_p): a higher ferrous concentration induces a slight increase k_p.

Then, Liou et al. [49] performed a series of UV only, UV/H_2O_2 and photo-Fenton reactions for the degradation of 0.01 mM TNT dissolved in ultra pure water ($[H_2O_2] = 0.29$ M, [Fe(II)] = 0.72 mM and pH 3.0). The results showed that the oxidation rates of TNT followed the sequence: 2.4 mW cm^{-2} UV only < 2.4 mW cm^{-2} UV/H_2O_2 < Fenton < photo-Fenton (2.4 mW cm^{-2} UV) < photo-Fenton (4.7 mW cm^{-2} UV). The authors studied also the effect of $[Fe^{2+}]$ and UV light on the TNT oxidation. In fact three concentrations of Fe^{2+} (1.44 mM, 2.88 mM and 4.32 mM) were applied for comparison between Fenton and photo-Fenton processes. It was observed that the degradation efficiency was promoted with either increasing Fe (II) concentration and/or by using a 2.4 mW cm^{-2} UV, simultaneously.

The degradation reaction rate of TNT followed once again a pseudo-first-order behaviour; and the authors concluded that increasing the intensity of UV light and the concentrations of ferrous ions promoted the oxidation rate under their experimental conditions.

Recently, Yardin and Chiron [50] studied the technical feasibility and performance of coupling flushing abilities of cyclodextrin (methylated-β-cyclodextrin, MCD) solutions for 2,4,6-trinitrotoluene (TNT) removal from contaminated soil. TNT in soil extract solution has been treated by photo-Fenton ($H_2O_2 = 30$ mM, $Fe^{2+} = 0.25$ mM, TNT = 0.43 mM). A value of 0.130 min^{-1} for k_{app} of TNT degradation reaction in distilled water was determined. Presence of dissolved natural organic matter (DOM) in the TNT soil extract solution obtained by soil flushing with distilled water resulted in inhibited degradation ($k_{app} = 0.081\ min^{-1}$) as compared to a distilled water TNT solution. This result was mainly due to hydroxyl radical scavenging properties of dissolved organic matter in soil extract solution obtained by soil flushing with cyclodextrins, the apparent rate constant has increased by a factor of 1.3 ($k_{app} = 0.175\ min^{-1}$) compared to what was observed with TNT degradation in distilled water. This experiment clearly shows that MCD increases TNT degradation rate

even in presence of a large excess of MCD and organic matter. Li et al. [51] determined the potential of combining Fenton oxidation with soil washing to remediate TNT-contaminated soil (0.52 M H_2O_2, 1.44 mM Fe^{2+} and pH 3.0). Complete destruction of TNT was achieved within 8 h for solutions containing <0.66 mM TNT and within 24 h for 0.8 mM and 0.92 mM TNT. First-order rate constant for TNT transformation ranged from 0.007 min^{-1} and 0.024 min^{-1}, depending on the initial concentration. More than 40% of the TNT was mineralized during 24 h by Fenton treatment. In contrast to Yardin and Chiron [50], when cyclodextrin is introduced, complete mineralization of soil extraction solutions was not achieved (60% of abatement of TOC value after 11 h oxidation).

Several authors focused on the ways to improve the rate of TNT degradation and the possibility to use solar technologies in order to reduce operating costs by minimizing the energy consumption [52,47,49,50]. In this case, the goals were to accelerate TNT degradation and promote a rapid oxidation of TNT intermediates without having the ability to detect all by-products, because of their accumulation and their rapid disappearance. In addition, the oxidation rates significantly increased with increasing the concentration of Fe (II), as well as illumination with UV light.

Based on the detailed and critical analysis of the existing literature on the TNT removal, photolysis process appears to be an effective oxidation technique but remains still expensive because of the need to use an energy source. The important operating parameters which affect the overall destruction and mineralization efficiency of the UV oxidation were both UV intensity and concentration of Fenton parameters. One can conclude that UV (21 W cm^{-1})/Fenton (H_2O_2 = 0.15 M and [Fe^{2+}] = 0.72 mM at pH adjusted to 3) was the best identified technology involving more than 95% of mineralization efficiency in 1 h treatment.

4.1.4. Photocatalysis with TiO_2

Photocatalytic or photochemical degradation processes are gaining importance in the area of wastewater treatment, since these processes result in complete organics mineralization with operation at mild conditions of temperature and pressure. There are good reviews available on this subject by [53–55] covering the analysis of the studies prior to 1995 and depicting basics of the processes including the oxidation mechanism of pollutants in details. The photo-activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution, with or without the presence of the catalyst. The radicals can be easily produced using UV radiation by the homogenous photochemical degradation of oxidizing compounds like hydrogen peroxide and ozone. An alternative way to obtain free radicals is the photocatalytic mechanism occurring at the surface of semiconductors (like titanium dioxide) and this indeed substantially enhances the generation rate of free radicals and hence the rates of degradation [56]. A major advantage of the photocatalytic oxidation based processes is the possibility to effectively use sunlight or near UV light [57–65] for irradiation, which should result in considerable economic savings especially for large-scale operations.

Dillert et al. [66] studied the TNT degradation in irradiated (λ = 320 nm) homogeneous solutions and in TiO_2 suspensions by varying the concentration of hydrogen peroxide and the pH, and showed that, in neutral and alkaline solution (absence of H_2O_2), 78% and 57% of the initial TNT have reacted within 2 h at pH 7 and 11, respectively. But with 0.1 mM of H_2O_2 72% and 56% of TNT have been degraded at the same pHs. However, in TiO_2 suspensions, the degradation rate is enhanced significantly compared with homogeneous solutions at all investigated pHs. Only at pH 11, a slight increase in reaction rate was observed with increasing concentrations of H_2O_2. Then it is important to note that the initial reaction rate of the photocatalytic degradation in the absence of H_2O_2 is hardly affected by the pH of suspension and addition of H_2O_2 to the suspension results in more pronounced effect of the pH on the reaction rate.

Schmelling and Gray [67] investigated the photocatalytic transformation and mineralization of TNT (initial experiments conditions TNT = 0.22 mM, O_2 = 40.0 mg L^{-1} and λ > 340 nm) in 250 mg L^{-1} TiO_2 slurries. The results demonstrate that TiO_2 photocatalysis using near UV radiation may be highly effective in the remediation of TNT-contaminated waters and can achieve almost complete mineralization. On the same outline, Son et al. [68] examined the effects of various parameters such as the initial TNT concentration and the initial pH, on the degradation rate in both presence of UV light illumination and TiO_2 catalyst. They concluded that the reaction rate also obeys to pseudo-first-order kinetics according to the Langmuir–Hinshelwood kinetic model, the percentage decreases in TNT concentration, resulting from the photolysis and photocatalytic reaction performed for 150 min, were 72% and 100%, respectively (after the same time period, the decreases in TOC concentrations were 40% and 80%).

Harmon [43] studied briefly the TNT photocatalytic demethylation by using tetraphenyl porphyrin sulfonate (TPPS). In fact, illumination of tetraphenyl porphyrin sulfonate TPPS, CuTPPS and FeTPPS in solution with 0.53 μM of TNT at pH 7 at room temperature using a tungsten lamp degrades TNT to trinitrobenzoic acid and trinitrobenzene. The rate of TNT degradation follows the series TPPS > FeTPPS > CuTPPS.

4.1.5. Advanced oxidation reactions with Ozone and ultrasound irradiation

Ozone is a very powerful oxidizing agent (E° = 2.07 V) able to react with most of the species containing multiple bonds (such as C=C, C=N, N=N, etc.), [69,70], but not with the single bonded functions, such as C–C, C–O, O–H at high rates. This is mainly due to the fact that there is no easy chemical pathway for the oxidation to take place. However, ozone does react with simple oxidizable ions such as S^{2-}, to form oxy-anions such as SO_3^{2-} and SO_4^{2-}. These oxidations are simple and the mechanisms only require contact of ozone with the ion. Consequently, the oxidation of these ions by ozone occurs rapidly. It is sometimes better to think of ozone as a highly reactive species capable of reacting with many species rather than just as a compound with a large reduction potential. This is because the practical action of ozone is often dependent on how it reacts with pollutants, and usually not in its ability to simply gain electrons (except in the case of simple ion oxidations). This idea emphasizes that an appropriate reaction pathway must exist for ozone to react with a substrate. In other words, although the thermodynamics for ozone induced oxidation may be favourable (due to ozone's high reduction potential), kinetic factors will most often dictate whether ozone will oxidize a pollutant in a reasonable time frame.

In this context and in the best of our knowledge only Wu et al. [44] have investigated the effects of some ions on TNT removal by O_3/H_2O_2 through the selection of HCO_3^-, $HCOO^-$, Cu^{2+} and Al^{3+}. In view of the kinetic constants, the authors concluded that HCO_3^-, $HCOO^-$ and Cu^{2+} have the ability of reducing of O_3/H_2O_2 efficiency with the following order $HCOO^- > HCO_3^- > Cu^{2+}$. However, Al^{3+} is an exception, because it has a potential to improve the efficiency. Also, when the two selected ions coexist, HCO_3^- and $HCOO^-$ inhibit the efficacy. The inhibition is greater than that of each one alone, and also greater than their sum. The inhibition of Cu^{2+} coexisting with $HCOO^-$ also is greater than that for each alone, but smaller than their sum. The integrated effect of Al^{3+} and $HCOO^-$ follows the addition effect.

Chen et al. [71] have employed O_3 and UV/O_3 to mineralize TNT in spent acid from toluene nitration process. According

Table 4
Summary of reaction conditions for TNT removal from water and soil solution by AOPs.

TNT	Reactions conditions	Some aspects of results	Elimination rate	References
Fenton and Fenton-like system				
0.5 mM	$[Fe^{2+}]$ = 1.25 mM, $[H_2O_2]$ = 0.625 mM, V = 0.5 L, pH 3	k_{app} of TNT = 0.034–0.038 min^{-1} range. K_{abs} = 9.6–10 × 10^8 M^{-1} s^{-1}	95% of TNT in 20 min	[40]
0.3, 0.2, 0.15, 0.1, 0.05 mM	$[Fe^{2+}]$ = 0.72 mM, $[H_2O_2]$ = 0.29 M at pH 3	k_{app} = 0.0085, 0.0096, 0.11, 0.14 and 0.21 min^{-1} for 0.3, 0.2, 0.15, 0.1, 0.05 mM TNT, respectively		[110]
0.65 mM (mixture of nitroaromatic compounds)	$[Fe^{2+}]$ = 0.06 M, $[H_2O_2]$ = 4 M at pH −1.4 (spent acid)			[39]
0.11 mM	2 M H_2O_2 (30%, w/v), iron minerals (2 g/L) at pH 7: hematite, ferrihydrite, lepidocrocite, goethite, magnetite, pyrite, green rust. EDTA = 10 mM, CMCD = 5 mM		40% of TNT in 23 h	[115]
0.11 mM	$[H_2O_2]$ = 80 mM, Fe^{2+} = 1.55 mM at pH 3; iron mineral = 1.76 g L^{-1} (hematite, ferrihydrite, lepidocrocite, goethite, magnetite, pyrite, green rust) at pH 6.8	k_{app} = 0.0348 min^{-1}	58% of TNT in 48 h	[42]
0.3 and 0.31 mM	$[Fe^{2+}]$ = 80 mg L^{-1}, 2% H_2O_2 at pH 3		Dark conditions: 40% of TNT in 24 h. Exposure light: >90% of TNT in 24 h	[51,52]
0.24 mM	H_2O_2/Fe^{2+} 5:1 (a-25 mM/5 mM and b-5 mM/1 mM)		95% of TNT under H_2O_2/Fe ratio 5:1	[112]
0.68 mM	H_2O_2/Fe^{2+} 5:1 (500/100 mg L^{-1}) at pH 3		95.5% of COD reduction	[113]
0.22 mM	7–30 mM of H_2O_2 (30%, w/v) and Fe^{3+} = 0.5 mM		100% of TNT in 2 h	[93]
0.3 and 0.31 mM	$[Fe^{2+}]$ = 80 mg L^{-1} and 2% H_2O_2 at pH 3	k_{app} = 71% higher at 45 °C than at room temperature (data not shown)	40% of TNT at 27 °C	[51]
400 mg kg^{-1}	2% (w/w) Fe^0, 1% H_2O_2, Fenton reagents (80 mg L^{-1}, 0.125% H_2O_2 or 0.2% CaO_2)			[111]
Direct and indirect photolysis with UV				
0.65 mM (mixture of nitroaromatic compounds)	$[Fe^{2+}]$ = 0.06 M, $[H_2O_2]$ = 4 M at pH −1.4 (spent acid), 12 low-pressure mercury vapour lamps (8 W each) at the wavelength 254 nm		78% of TOC in 6 h at 343 K under UV/Fenton. 72% of TOC under UV/H_2O_2	[39]
0.88 mM	$[Fe^{2+}]$ = 0.25 mM, $[H_2O_2]$ = 30 mM at pH 3. Mercury lamp (150 W) at wavelength 254 nm, [MCD] = 5 mM	k_{app} = was 0.13 min^{-1} in distilled water	95% of TOC in 4 h in distilled water. 60% of TOC in 11 h in soil flushing	[50]
10^{-5} M	$[Fe^{2+}]$ = 0.72 mM, $[H_2O_2]$ = 0.29 M at pH 3, eight low-pressure mercury lamps of 10 W:2.4 mW cm^{-2} and 4.7 mW cm^{-2}	k_{app} = 0.002, 0.007, 0.014, 0.025, and 0.037 min^{-1}. for 2.4 mW cm^{-2} UV, 2.4 mW cm^{-2} UV/H_2O_2, Fenton, 2.4 mW cm^{-2} UV/Fenton and 4.7 mW cm^{-2} UV/Fenton respectively		[49]
0.42 mM	$[Fe^{2+}]$ = 0.36 mM, 1.44 mM, $[H_2O_2]$ = 0.29 M at pH 3, light source: 40 W ultraviolet lamp with peak wavelength of 254 nm	k_{app} = 0.0359 and 0.0918 min^{-1} for 0.360 and 1.44 mM of Fe (II), respectively		[47]
3 × 10^{-4} mM	$[H_2O_2]$ = 10, 50, 100 and 300 mg L^{-1} at 40 W m^{-2} UV radiation intensity		40% of TOC in 30 min. 80% of decolorization in 30 min at (UV/H_2O_2 = 10 mg/L and pH 6.5)	[45]
0.31 mM	1.8 < Fe < 28.6 mM (as pyrite), $[H_2O_2]$ = 0.015–0.029 M Classic Fenton (1.8 mM of Fe(II) as ferrous iron + 0.029–0.29 M H_2O_2 at pH 3. Artificial light source of 200 W	k_{app} = 0.06, 0.13, 0.23, 0.29, 0.57, 0.82 h^{-1} for 1.8, 3.6, 5.4, 7.2, 14.4, 28.8 of Fe^{2+} and 0.015 M of H_2O_2. k_{app} = 0.05, 0.14, 0.25, 0.31, 0.49, 0.78 h^{-1} for 1.8, 3.6, 5.4, 7.2, 14.4, 28.8 of Fe^{2+} and 0.029 M of H_2O_2		[114]
500 mg kg^{-1} ∼ 0.31 mM	$[Fe^{2+}]$ = 0.72 mM and 0.15 M, $[H_2O_2]$ = 0.29 M at various pHs 3, 5.7 and 6, and 21 mW cm^{-2} UV radiation intensity	k_{app} = 0.04, 0.031 and 0.017 min^{-1} for UV/Fenton at pH 3, dark Fenton and UV/Fenton	95% of TOC in 24 h in UV medium. 45% of TOC in 24 h under dark-Fenton system	[46]

Table 4 (*Continued*)

TNT	Reactions conditions	Some aspects of results	Elimination rate	References
Photocatalytic processes				
0.53 μM	0.05 M sodium phosphate buffer at pH 7 with 16 μM TPPS, 10 μM FeTPPS, or 10 μM CuTPPS and 3×10^{-4} W cm^{-2} UV radiation			[43]
0.13 mM	[TiO_2] = 1.0 g/L, UV = 8.2 mW cm^{-2} (254 nm) at pH 7		40% of TNT in 150 min under photolysis. 80% of TNT in 150 min under photocatalysis	[68]
0.175 mM	[O_2] = 40 mg/L, radiation > 340 nm and [TiO_2] = 250 mg L	k_{app} = 2.5 h^{-1} with TiO_2 and k_{app} = 1.2 h^{-1} with absence of TiO_2	92% of COD in aerobic conditions using TiO_2-light >340 nm	[67]
0.1 mM	TiO_2 = 1.0 g L^{-1}, 0 < H_2O_2 < 1 mM, 3 < pH < 11			[66]
0.22 mM	[O_2] = 40 mg L^{-1}, radiation > 340 nm, [TiO_2] = 250 mg L^{-1}, bicarbonate (10–100 mM), nitrate (10 mM), chloride (10 mM) at 5.5 < pH < 7.5	k_{app} = 5, 5.2, 5.1, 4.8, 3.9, 4.9 h^{-1} for no salt, nitrate (10 mM), chloride (10 mM), bicarbonate (10 mM), bicarbonate (100 mM), borate (10 mM), respectively		[116]
0.13 mM	[TiO_2] = 1.0 g L^{-1}, (4 UV lamps and 5 photo-reactors columns) with a 40 W at 254 nm. pH at 3, 5 and 7	k_{app} = 0.0173, 0.0422, 0.0451 min^{-1} at pH 3, 5, 7, respectively. k_{app} was the fastest at pH 11	82% of TNT in 150 min at pH 7 with [TiO_2] = 1.0 g L^{-1}	[117]
Ozone and ultrasound irradiation processes				
0.13 mM	1.19 < [HCO_3^-] < 3.54 mol L^{-1}, 10^{-4} < [$HCOO^-$] < 2×10^{-4} mol L^{-1}, 3.13×10^{-3} < [Cu^{2+}] < 3.125×10^{-2} mol L^{-1} and 2×10^{-3} < [Al^{3+}] < 8.06×10^{-3}			[44]
–	Ultrasonic frequency = 20 and 500 kHz	k_{obs} = 1.67×10^{-5} s^{-1} with O_2, 4.5×10^{-5} s^{-1}, with (Ar) and 1.88×10^{-4} s^{-1} with O_2/O_3. At 500 kHz k_{obs} = 2×10^{-5} s^{-1} with O_2, 7.17×10^{-5} s^{-1}, with (Ar) and 8.5×10^{-5} s^{-1} with O_2/O_3		[75]
1 mM (calculated from available data)	Spent acid medium (mixture of nitroaromatic compounds) at pH −1.4, 12 low-pressure mercury vapour lamps (8 W each) at 254 nm. 0 < O_3 < 3.8 g h^{-1}. (UV/O_3/Fe^{2+}): 0 < Fe^{2+} < 0.1 M		Complete TNT removal under UV/O_3 (96 W/3.8 g h^{-1} and T°C = 212 K) conditions (data not shown)	[71]
Electrochemical processes				
0.3 mM	Salt concentration [Na_2SO_4] = 36 g L^{-1}, pH 8, applied current: I = 23–65 mA, electrode: glassy carbon (67.5 cm^2) and dissolved oxygen: 0.2 mg L^{-1} (anoxic), 8.4 mg L^{-1} (oxic)		An approximate 60–100% of TNT under oxic conditions	[76]
0.3 mM	Electrolyte solution 6–9 mM of Na_2SO_3 in the anode (platinium wire) compartment of the reactor, glassy carbon (cathode), I = 75–300 mA at pH 8		85–92% of TNT with two electrolytes sodium sulphate and lithium sulphate at 3.53 mM	[77]
4×10^{-3} to 0.088 mM	New type of electrode (tin carbon particles) [NaCl] = 0.5 M			[118]
0.12 and 0.22 mM	Electrochemical assisted photocatalytic degradation of TNT with TiO_2-biased at +1.1 V vs. NHE at wavelength >340 nm and pH 5.1. Cds:TiO_2 as coupled photocatalysts	k_{app} = 1, 0.87, 0.93, 0.93 h^{-1} for 0, +0.1, +0.6, +1.1 (V/vs. NHE), respectively		[119]
Spent acid (mixture of nitroaromatic compounds, TNT concentration not given)	0 < O_2 < 140 mL min^{-1}, 0 < Fe^{2+} < 300 mg L^{-1}, 50 < H_2SO_4 < 74 (wt%) and EP/voltage = 6 V (The batch wise mode under atmospheric pressure both cathode and anode plates were made of corrosion-resistant platinum of 99.9% purity with 2.0 cm × 2.0 cm × 0.1 cm)		Complete mineralization of TNT under the conditions of cell voltage = 6 V, T = 343 K, O_2 = 120 ml min^{-1} and Fe^{2+} = 100 mg L^{-1} (data not shown)	[100]

Table 4 (*Continued*)

TNT	Reactions conditions	Some aspects of results	Elimination rate	References
Spent acid (mixture of nitroaromatic compounds, TNT concentration not given)	$0 < O_2 < 140\,mL\,min^{-1}$, $0 < Fe^{2+} < 300\,mg\,L^{-1}$, $323 < T^{\circ}C < 343\,K$, $50 < H_2SO_4 < 74$ (wt%) and $2 < EP/voltage < 8\,V$ (a batch wise mode under atmospheric pressure: both cathode and anode plates were made of corrosion-resistant platinium of 99.9% purity with 2.0 cm × 2.0 cm × 0.1 cm)		Complete mineralization of TOC can be achieved under the conditions of cell voltage = 6 V, T = 343 K, O_2 = 120 ml min^{-1} and H_2SO_4 = 50 wt% (data not available)	[89]
0.2 mM	$[Fe^{3+}]$ = 0.2 mM, $60 < I < 250$ mA, electrolyte Na_2SO_4 = 50 mM, pH 3 (glassy carbon for cathode) (60 cm^2 and anode platinium)	k_{app} = 0.26, 0.38, and 0.54 min^{-1} for 60, 100 and 250 mA, respectively	90% of TNT was achieved after 6 h of treatment	[90]

to these authors, nearly complete mineralization of TNT can be achieved by ozonation (3 g h^{-1} combined with UV = 96 W intensities sources at the wavelength of 254 nm). Nevertheless, they concluded that hydroxyl radicals would not be generated by either ozone decomposition or photolysis of ozone under these experimental conditions.

However, the ultrasonic irradiation consisting in introducing a high power ultrasound (i.e., sound energy with frequencies in the range 15 kHz to 1 MHz) into liquid reaction mixtures is known to cause a variety of chemical transformations [72]. The chemical effects of ultrasound on chemical reaction were first reported by Richards and Loomis [73]. This early report was followed by a detailed investigation of the catalytic effect of ultrasonic irradiation on the auto-oxidation of iodide ion [74]. Since then the application of ultrasound on chemical as a catalyst in chemical synthesis has become an important field of research. For instance, Hoffmann et al. [75] investigated the ultrasonic irradiation for the degradation of chemical contaminants in water and showed that the sonochemical TNT degradation (no concentration reported) followed an apparent pseudo-first-order rate, which varied with the nature of the dissolved gases and the ultrasonic frequencies. In fact, at 20 kHz, $k_{obs} = 1.67 \times 10^{-5}\,s^{-1}$ with O_2, $4.5 \times 10^{-5}\,s^{-1}$, with (Ar) and $1.88 \times 10^{-4}\,s^{-1}$ with O_2/O_3. However, the rates constants registered at 500 kHz are $k_{obs} = 2 \times 10^{-5}\,s^{-1}$ with O_2, $7.17 \times 10^{-5}\,s^{-1}$, with (Ar) and $8.5 \times 10^{-5}\,s^{-1}$ with O_2/O_3. Ultrasonic irradiation at 500 kHz yielded consistently higher degradation efficiencies than 20 kHz irradiation for all background gases.

4.1.6. Advanced oxidation process with electrochemical reactions

Doppalapudi et al. [76] and Palaniswamy et al. [77] studied the TNT electrochemical reduction and performed several experiments to evaluate the process efficiency. Indeed, they showed that the electrochemical processes can be successfully used for TNT reduction and readily taking place under both oxic and anoxic conditions. The kinetic rates increased with the increase in current, but at higher density currents (0.79 mA cm^{-2} and 0.96 mA cm^{-2}), mass transfer rates governed the reduction rates under both oxic and anoxic conditions.

However, in the last years the indirect electro-oxidation method known as electro-Fenton was developed for wastewater remediation [78–82]. It consists in the continuous supply of H_2O_2 to an acidic contaminated solution from the two-electron reduction of O_2 gas at a carbonaceous cathode:

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (7)$$

Thus H_2O_2 generated reacts with Fe^{2+} present in the solution to produce hydroxyl radical ($OH^{\bullet}$) and Fe^{3+} by means of Fenton's reaction (8) with a second-order rate constant (k_8) of 63 $M^{-1}\,s^{-1}$ [83]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (8)$$

$OH^{\bullet}$ is the second strongest oxidizing agent known after fluorine and can react rapidly with organic pollutants with k_8-values of 10^8–$10^{10}\,M^{-1}\,s^{-1}$, yielding dehydrogenated or hydroxylated products up to total mineralization into CO_2, water and inorganic ions. The Fe^{3+}/Fe^{2+} system is catalytic, since Fe^{2+} can be regenerated mainly from the reduction of Fe^{3+} at the cathode from reaction (9) [84], and in smaller extent by H_2O_2 from reaction (10) with $k_{10} = 8.4 \times 10^{-6}\,M^{-1}\,s^{-1}$ [85], by hydroperoxyl radical ($HO_2^{\bullet}$), a weaker oxidant than $OH^{\bullet}$ from reaction (11) with $k_{11} = 7.8 \times 10^5\,M^{-1}\,s^{-1}$ [86] and/or by organic radical intermediates $R^{\bullet}$ from reaction (12):

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (9)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (10)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \quad (11)$$

$$R^{\bullet} \rightarrow Fe^{2+} + R^+ \quad (12)$$

However, a part of $OH^{\bullet}$ is lost by its direct reaction with Fe^{2+} from reaction (13) with $k_{13} = 3.2 \times 10^8\,M^{-1}\,s^{-1}$ [87] and with H_2O_2 from reaction (14) with $k_{14} = 2.7 \times 10^7\,M^{-1}\,s^{-1}$ [88]. The rate of Fenton's reaction (8) [75] may also decay by oxidation of Fe^{2+} in the presence of HO_2°, as shown in reaction (15) with $k_{15} = 1.2 \times 10^6\,M^{-1}\,s^{-1}$ [86]. This can also be noted for the anode (reaction (16)) when an undivided cell is used:

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \quad (13)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (14)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^- \quad (15)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (16)$$

In this context, Chen and Liang [89] studied the TNT decomposition by electro-Fenton oxidation. The electrolytic experiments were carried out to elucidate the influence of various operating parameters on the performance of mineralization of TOC in spent acid, including reaction temperature, additions of oxygen, sulfuric acid concentration and ferrous ions. According to these authors, electro-Fenton's reagent was verified to be an effective oxidant for mineralization of TNT. Besides, it is remarkable that the nearly complete mineralization of TOC can be achieved under the conditions of cell voltage = 6 V, T = 343 K, O_2 = 120 mL min^{-1} and $[Fe^{2+}]$ = 100 mg L^{-1}, which abate partial amounts of water of spent acid simultaneously. This method reveals that the electrolytic technique established may be utilized to regenerate spent acid in practice. In the same way, Murati et al. [90] investigated the effect

of the current on the 0.2 mM of TNT degradation and observed a complete one after 20 min under 60 mA. TOC removal was achieved after 8 h treatment. The pseudo-first-order reaction rate constants, k_{app}, were calculated from linear regression of the pseudo-first-order kinetic model with related coefficients higher than 0.98. For the three current intensities investigated, rate constants of 0.26 min^{-1}, 0.38 min^{-1} and 0.54 min^{-1} were found respectively for 60 mA, 100 mA and 250 mA.

Throughout this review, it was found that differences in the applied experimental conditions in different studies process are the principle reasons for variations in final outputs and conclusions. Although descriptive experimental features of the papers discussed in Section 4 have already been specified in the text, a comparative list of all is given in Table 4. This latter show that a slight variation of the apparent rates is more than obvious and this difference is due to the difference in operating conditions used (concentration iron, H_2O_2, the use of UV radiation and TNT concentration). Apparent rates range found by Ayoub et al. [40] under Fenton (0.034–0.038 min^{-1}) is similar to that in UV/Fenton of Liou et al. [47] and Li et al. [46] (0.036 min^{-1} and 0.04 min^{-1}, respectively) and to Fenton-like system, Matta et al. [42] (0.0348 min^{-1}). But these values are different from what was found by electro-Fenton process according to Murati et al. [90]. In fact, apparent rate of 0.38 min^{-1} 10 times higher was obtained when applying 100 mA, therefore, TNT degradation was faster. However, these rates are completely different from those obtained using a biological process; indeed, Brannon and Myers [91], cited in a report addressed to US Army Corps of Engineers, presented that the first-order rate coefficients of TNT were 8.84×10^{-4} min^{-1} and 2.76×10^{-4} min^{-1} for TNT abiotic and biotic, respectively under aerobic degradation conditions, and were of 8.83×10^{-4} min^{-1} and 0.001 min^{-1} for TNT abiotic and biotic respectively under anaerobic degradation conditions. Thus, these results confirm those cited in the literature, about the slowness of the biological treatment for TNT removal.

Furthermore, we can observe that in the majority of the works, more than 71% of TNT removal was achieved using photolysis, photocatalysis, Fenton, UV/Fenton and electro-Fenton. Regarding Table 4, electro-Fenton and electrochemical reduction processes appear to be only effective for the TNT mineralization (92% and 95% for the reduction and electro-Fenton, respectively).

5. Overview of degradation by-products

One of the major concerns with TNT destruction by AOP are the final oxidation products, because in some cases the products might still exert endocrine activity and/or might be more toxic than the parent compound [92].

Indeed, the SPE LC–MS–MS analysis made by Ayoub et al. [40], under Fenton process revealed four aromatic intermediates: 2,4,6-trinitrobenzaldehyde; 2,4,6-trinitro-cyclohexa-2,4-dienol, 2,4,6-trinitrobenzylalcohol and dinitro-hydroxy-benzaldehyde isomers. It is worth noting that these authors did not detect any trinitrobenzoic acid or trinitrobenzene compounds as compared with owned standards. It was previously demonstrated that the two last compounds resulted from a further degradation of trinitrobenzaldehyde ([39,49]) and it may be hypothesized that these compounds (or their NO_2/OH substituted analogs) could be formed later. Furthermore, picric acid or reduction products (e.g., amino-ones) were not observed in conditions mentioned above, although cited by other authors under various AOPs. Fig. 2 summarizes all the by-products found by Fenton and combined metallic iron and Fenton processes. No similarity was observed between these by-products obtained in each case. This can be attributed to the fact that, in the case of combined processes, the first step is the reduction of nitro groups and not the TNT oxidation which is the case in the Fenton process.

The formation of active intermediates from the Fenton-like reagent (a mixture of iron (III) ions and hydrogen peroxide) in aqueous or soil solutions has been also studied. In fact, Hess et al. [93] have tentatively identified, by electrospray ionization tandem mass spectrometry (ESI-MS–MS), hydroperoxide adducts as: 4,6-dinitro-*o*-cresol (DNOC); subsequent oxidation leads to 3,5-dinitropheny-6-methylene-1-one. Another pathway was studied and consisted in obtaining trinitrobenzene, which oxidized to form TNB-hydroperoxide. After that, a sequential denitration leads to dinitrophenol followed by dihydroxynitrobenzene. The third denitration of the last product forms a phloroglucinol. This research provides further evidence for the existence of reduced oxygen radical species apparently responsible for the degradation of highly oxidized organic compounds, the result was confirmed by Ayoub et al. [40].

Under the same reagent (Fenton-like), the analyses by LC/MS in negative electrospray ionization mode, performed by Matta et al. [42] revealed the presence of 4 major by-products. Oxidative degradation of TNT involves a hydroxyl radical attack on the C1 of TNT. The resulting radical which is stabilized by resonance might evolve in two different ways. The first possibility would be a dimerization. The second possibility would be the formation of an epoxide followed by further hydroxylation of the aromatic ring prompting ring opening (see Fig. 3 for details). All these methods (Fenton-like systems) have been successfully used for the total degradation of TNT and it has been also shown that different and non-exhaustive mechanisms were involved during TNT degradation.

According to Liou et al. [47] the TNT degradation pathway using UV/Fenton process is expected to proceed in three phases: the first phase is the methyl group oxidation of TNT. The second phase is the decarboxylation of the aromatic acid, a mechanism that was previously reported by Urbanski [94]. The last phase is hydrolysis and mineralization of nitro groups on the aromatic ring, as reported by March [95] (see Fig. 4).

The TNT degradation mechanism, initiated by Liou et al. [49] in aqueous medium revealed five by-products, as TNB, dinitrotoluene (DNB), dinitrobenzoic acid (DNBA) and dinitrobenzene (DNB). Further oxidation involved the cleavage of aromatic ring and could be degraded gradually into final products of aliphatic organic acids, water and carbon dioxide, also reported by Zoh and Stenstrom [96] (see Fig. 4).

Using UV/Fenton, the TNT degradation pathway has been elucidated by Yardin and Chiron [50]. After successive TNT hydroxylations, oxidative opening of the TNT aromatic ring quickly occurred, leading to the accumulation of short chain of carboxylic acids such as oxalic acid and formic acid. LC/MS analysis in negative electrospray ionization mode revealed four major by-products. The by-product 1 was identified as 2,4,6-trinitrophenol after methyl substitution by alcohol moieties. Further hydroxylation led to the formation of the second by-product as 3-hydroxy-2,4,6-trinitrophenol. Finally an oxidative aromatic ring opening reaction at the level of the C–C bonds between adjacent hydroxyl and nitro groups leads to the formation of aliphatic compounds, mainly oxalic acids. As shown in Fig. 4, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene are the major by-products identified under photo Fenton process (see Fig. 4).

According to Schmelling and Gray [67], the TNT photocatalytic transformation involved both oxidative and reductive steps: trinitrobenzoic acid, trinitrobenzene and trinitrophenol were observed as oxidative intermediates species and 3,5-dinitroaniline was identified as a reduction product. However, the mechanism established by these authors (Fig. 5) indicates that only benzaldehyde and benzoic acid moieties have been reproduced and no reductive product has been reported as was presented in their work.

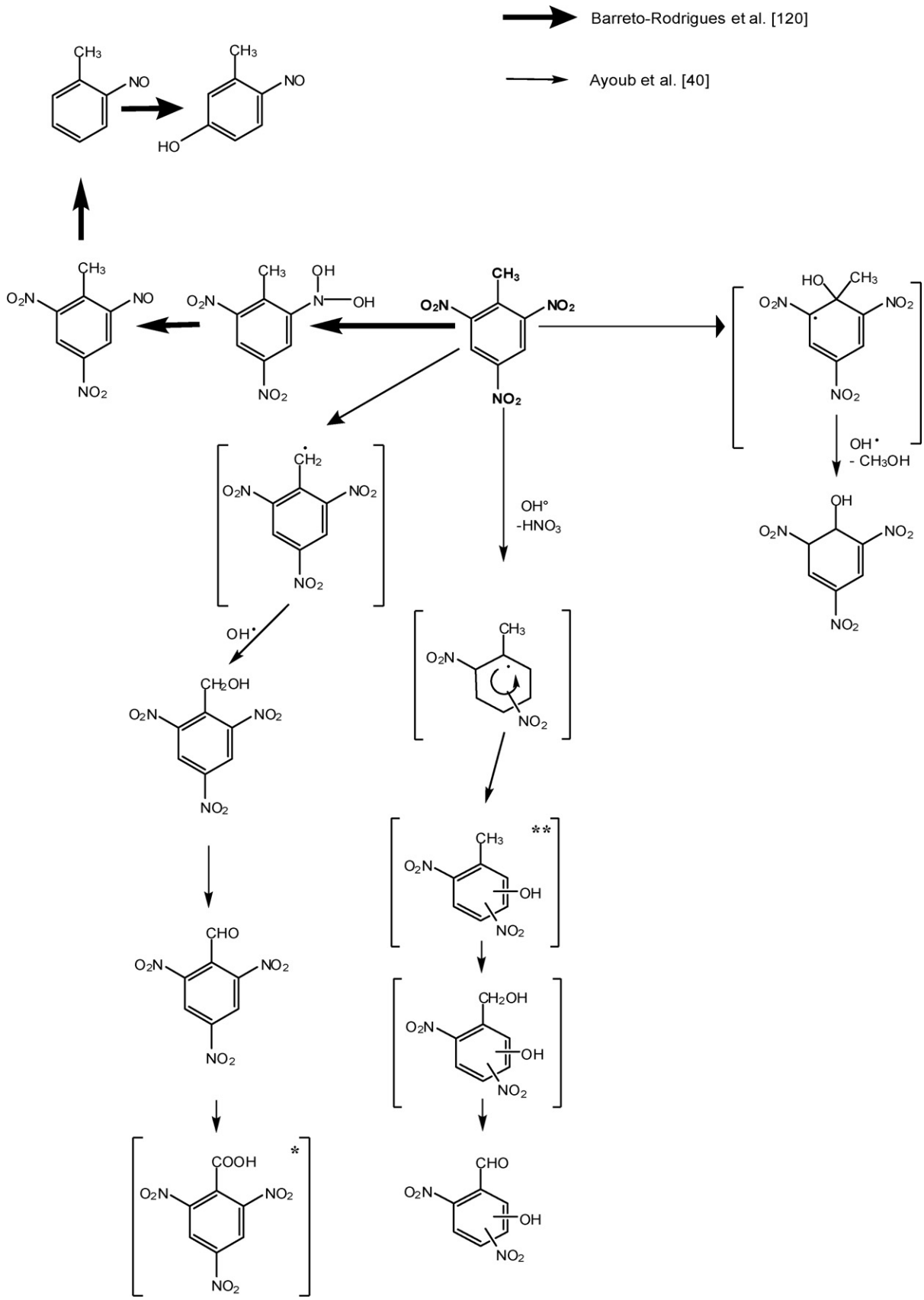

Fig. 2. Mechanisms degradation of TNT under Fenton process.

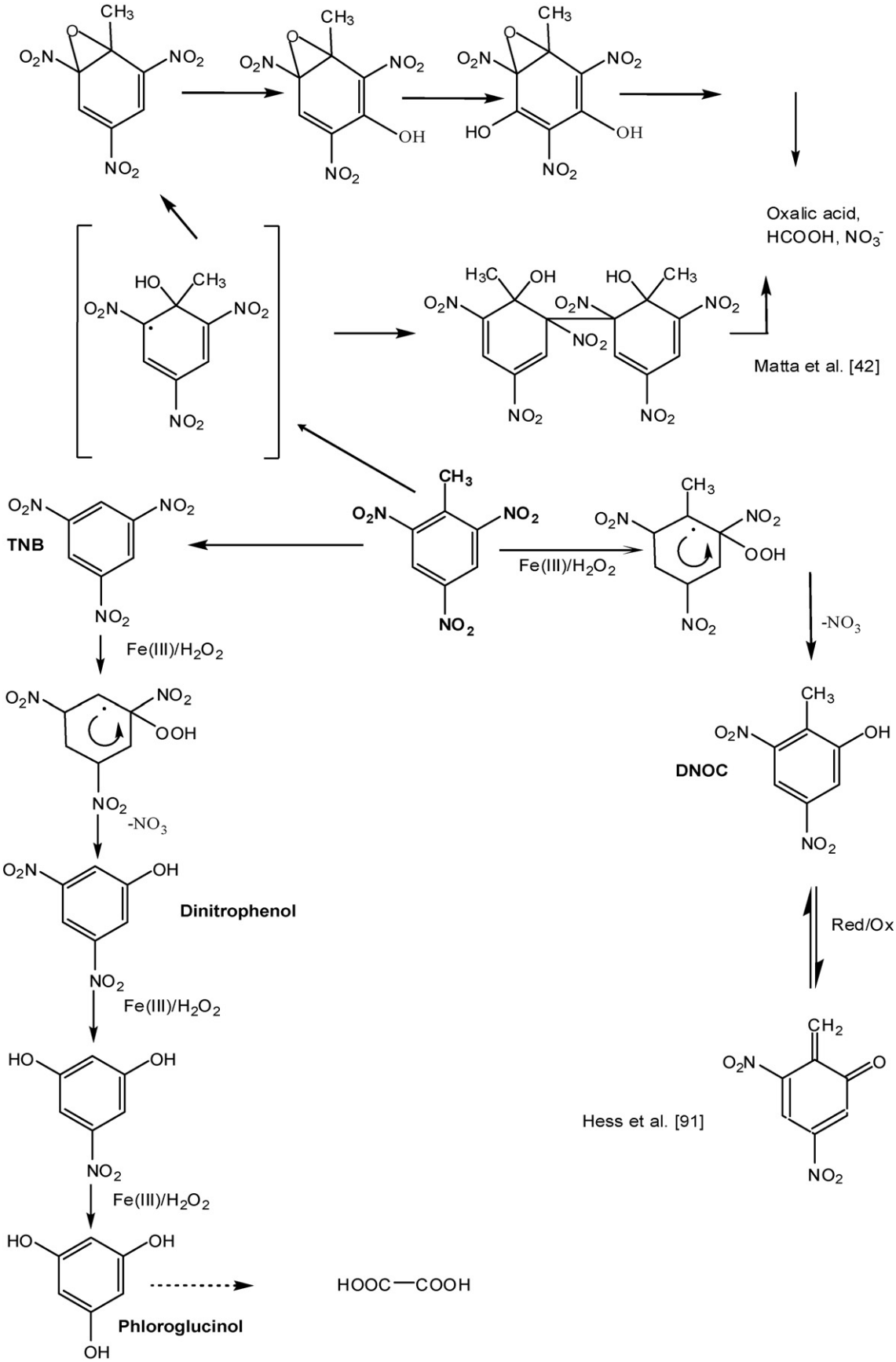

Fig. 3. Proposed degradation pathways of TNT by modified Fenton reaction.

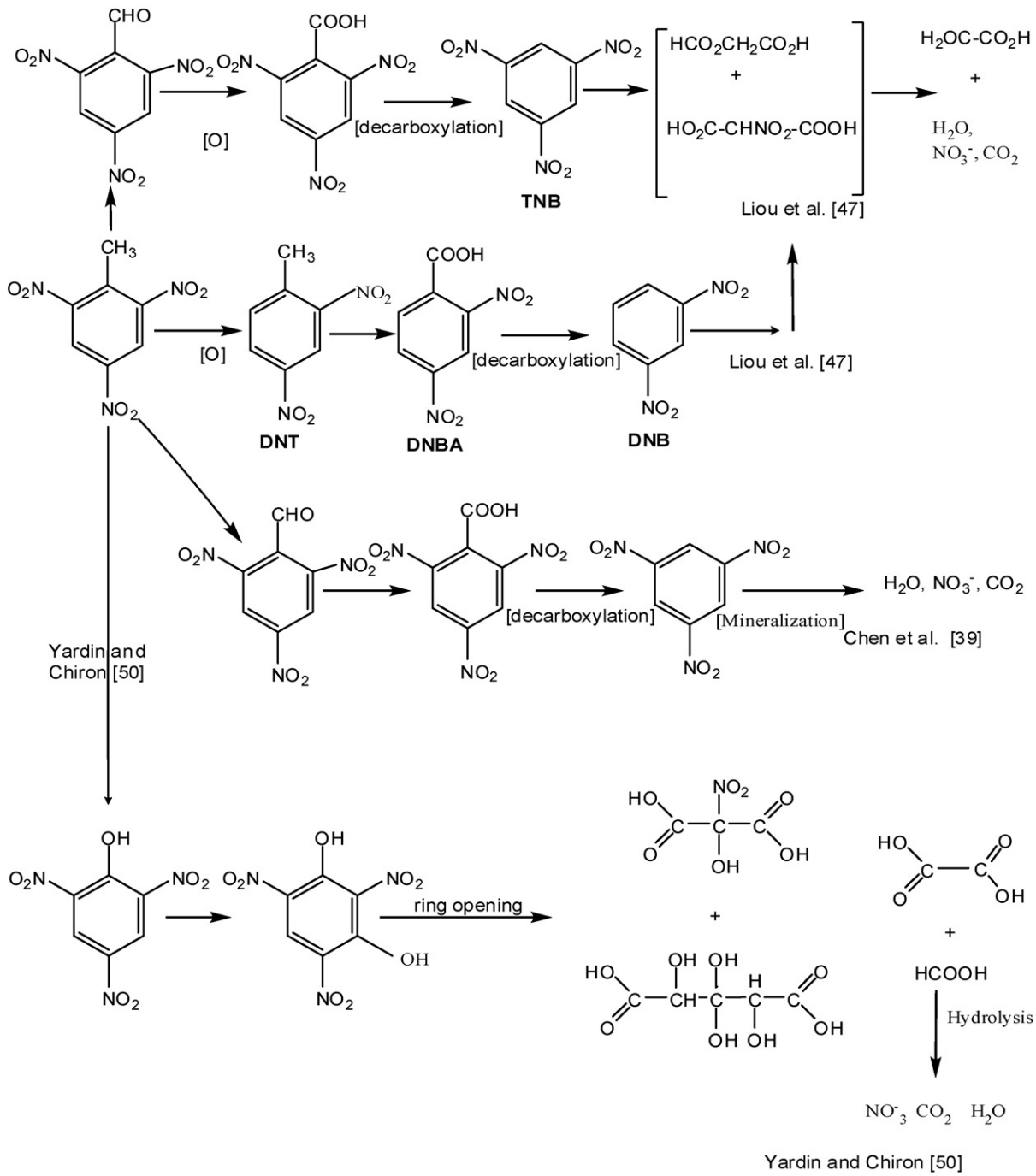

Fig. 4. Mechanisms degradation of TNT under photo-Fenton process.

Moreover, Son et al. [68] did not identified aromatic intermediate compounds but only acetate and formate. NO_3^- constitutes the major by-products of both TNT photocatalysis and photolysis.

Thus one can observe in Table 5 that the main photocatalytic TNT degradation studies have been focused on comparing the rate between TiO_2 and UV/TiO_2 and the general pathways proposed remained classical and likely incomplete. However, Chen et al. [67] could identified 2,4,6-trinitrobenzoic acid, 2,4,6-trinitrobenzaldehyde, 1,3,5-trinitrobenzene as the main by-products under UV/O_3 process (see Fig. 6).

Hoffman et al. [75] used ultrasonic irradiation and reported also, that trinitrobenzoic acid and trinitrobenzene (see Fig. 7), after a pyrolytic decarboxylation, were the major removal by-products based on LC/MS analysis. However, the removal TNT study remained incomplete and like all the others studies; the mechanism was not extensively studied.

Doppalapudi et al. and Planiswamy et al. [76,77] concluded that the end-products identified for the electro chemical reduction, may reach 60–100% for the molar balance removal. These species are: two kinds of azoxy dimers and various amino substitutes like 2-amino-4,6-dinitrotoluene, 2,6-diamino-4-nitrotoluene, 4-amino-2,6-dinitrotoluene and 2,4-diamino-6-dinitrotoluene. As shown in Fig. 8, different ways have been reported, the reduction of nitro groups in NHOH and NH_2 and those of dimerization.

According to Chen and Liang [89], the plausible mineralization pathways of organic compounds by electro-Fenton oxidation are suggested as follows. Firstly, the denitratation of TNT results in 2,4-DNT and/or 2,6-DNT, of which nitro group is cleaved to form

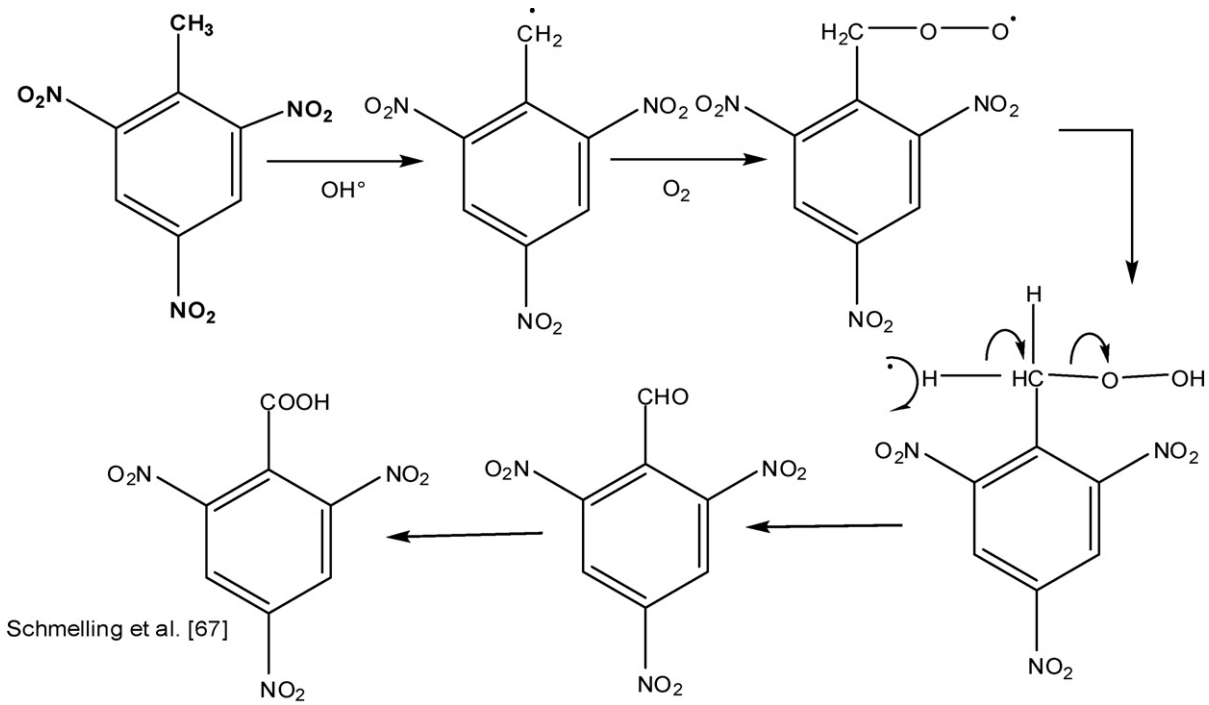

Fig. 5. Reaction pathway for TNT oxidation under photocatalytic conditions.

Table 5
Identified by-products of TNT oxidation by various AOPs.

AOP method	By-products	References
Fenton	2,4,6-Trinitrobenzylalcohol and 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitro-cyclohexa-2,4-dienol and dinitro-hydroxy-benzaldehyde isomers	[40]
Fenton	2,4,6-Trinitrobenzaldehyde, 2,4,6-trintrobenzoic acid, and 2,4,6-trinitrobenzene	[39]
Fenton	2,4,6-Trinitrobenzoic acid and 2,4,6-trinitrobenzene	[51,52]
Fe^0 and Fenton	Triaminotoluene	[112]
Fe^0 and Fenton	2-Nitrous-toluene and 2-nitrous-5-hydroxyl-toluene	[113]
Fenton like	Dimers of 1-hydroxy-2,4,6-trinitrotoluene, epoxide of 2,4,6-trinitrotoluene.	[42]
Fenton like	4,6-Dinitro-o-cresol (DNOC), 3,5-dinitrophenyl-6-methylene-1-one, TNB-hydroperoxide, dinitrophenol, dihydroxynitrobenzene, phloroglucinol (1,3,5-trihydroxybenzene).	[93]
UV/Fenton	2,4,6-Trinitrophenol, 1,3-dihydroxy-trinitrotoluene, oxalic and formic acid	[50]
UV/Fenton	2,4,6-Trintrobenzoic acid, 2,4,6-trinitrobenzene, 2,4-dinitrobenzoic acid 2,4-dinitrobenzene, formic and oxalic acids	[49]
UV/Fenton	2,4,6-Trintrobenzaldehyde 2,4,6-trintrobenzoic acid, 2,4,6-trinitrobenzene and oxalic acid	[47]
Photocatalysis by porphyrins	2,4,6-Trinitrobenzoic acid and 2,4,6-trinitrobenzene	[43]
Photocatalysis with TiO_2 slurries	In aerobic conditions: 2,4,6-trinitrophenol, 2,4,6-trinitrobenzene, 2,4,6-trinitrobenzoic acid and 3,5-dinitroaniline. In anaerobic conditions: NO_3^-, NO_2^- and NH_4^+	[67]
Photocatalysis with TiO_2 in the presence of H_2O_2	2,4,6-Trinitrobenzene	[66]
UV/O_3	2,4,6-Trinitrobenzaldehyde, 2,4,6-trinitrobenzoic acid and 2,4,6-trinitrobenzene	[71]
Ultrasonic irradiation	2,4,6-Trinitrobenzoic acid and 2,4,6-trinitrobenzene	[75]
Electrochemical reduction	Under anoxic conditions: 2,6-diamino-4-nitrotoluene, 4-amino-2,6-dinitrotoluene, 2,4-diamino-6-nitrotoluene, 2,2′,4,4′-tetranitro-6,6′-azoxytoluene and 4,2′,6,6′-tetranitro-2,4′-azoxytoluene Under oxic conditions: 2-amino-4,6-dinitrotoluene 4-amino-2,6-dinitrotoluene, 2,2′,4,4′-tetranitro-6,6′-azoxytoluene and 4,2′,6,6′-tetranitro-2,4′-azoxytoluene	[76]
Electrochemical reduction	2,6-Diamino-4-nitrotoluene, 4-amino-2,6-dinitrotoluene, 2,4-diamino-6-nitrotoluene, 2-amino-4,6-dinitrotoluene, 2-hydroxylamino-4,6-dinitrotoluene, 4-hydroxylamino-2,6-dinitrotoluene, 2,4,6-triaminotoluene, 2,2′,6,6′-tetranitro-4,4′-azoxytoluene 4,2′,6,6′-tetranitro-2,4′-azoxytoluene and 2,2′,4,4′-tetranitro-6,6′-azoxytoluene	[77]
Electrochemical reduction	**Pathway 1**: 2-nitroso-4-hyroxlamino-6-nitrotoluene, 2-amine-4-nitroso-6-hdroxylaminotoluene, triaminotoluene **Pathway 2**: 4,6-dinitro-2-aminotoluene, 2,4-amino-6-nitrotoluene and triaminotoluene	[118]
Electrochemical assisted photocatalytic degradation	2-Amino-4,6-dinitrotoluene; 4, amino,2-6, dinitrotoluene; 1,3,5-trinitroibenzene; 3, 5-dinitroaniline.	[119]
Electro-Fenton	2,4-DNT and/or 2,6-DNT, *o*-mononitrotoluene, toluene, benzaldehyde and benzoic acid.	[100]
Electro-Fenton	2,4-DNT and/or 2,6-DNT, *o*-mononitrotoluene, toluene, and benzoic acid.	[89]

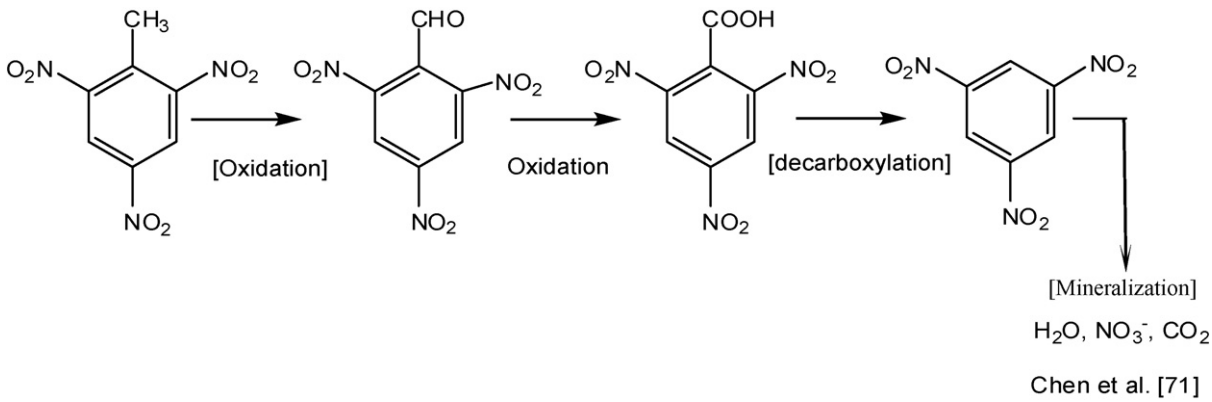

Fig. 6. Reaction pathway for TNT oxidation under photo-ozonation conditions.

o-MNT. Subsequently, *o*-MNT is denitrated into toluene, which is successively oxidized to benzaldehyde. Finally, the decarboxylation of benzoic acid and the mineralization procedures followed lead to ultimate products of carbon dioxide, nitrate ion and water (see Fig. 9).

Also Murati et al. [90] have used Electro-Fenton for TNT degradation, however, the research paper of these authors is incomplete and the study by HPLC-DAD did not succeed to identify any TNT intermediates.

In summary the list of by-products formed, display in Table 5, shows that trinitrobenzoic acid and trinitrobenzene were the two most commonly observed by-products regardless of the AOPs techniques. It was proposed that the initial step in the reaction mechanism of Fenton, photo Fenton or photocatalytic transformation with TiO_2 processes was the methyl group oxidation followed by $OH^{\bullet}$ attack to form after a decarboxylation the trinitrobenzene. Further oxidation of these intermediates produces a short and long chain structures leading finally to oxalic, formic and acetic acids [39,42,47,49,50,97–99].

According to Table 5, it is interesting to note that the similarities were observed in the degradation by-products by electrochemical reduction and biological degradation (2,6-diamino-4-nitrotoluene; 4-amino-2,6-dinitrotoluene, 2,4-diamino-6-nitrotoluene, 2-amino-4,6-dinitrotoluene, 2-hydroxylamino-4,6-dinitrotoluene,

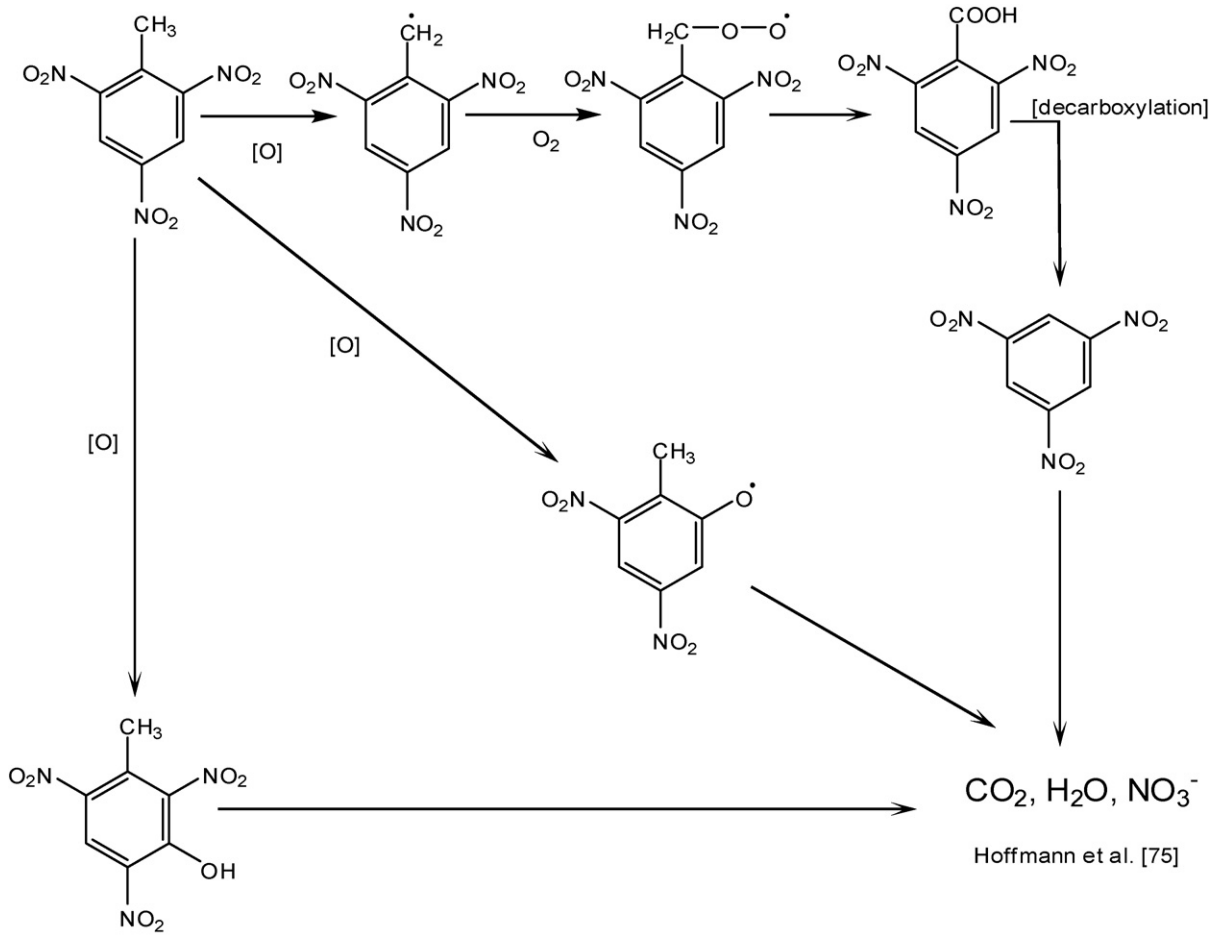

Fig. 7. Degradation mechanisms of TNT by ultrasound irradiation.

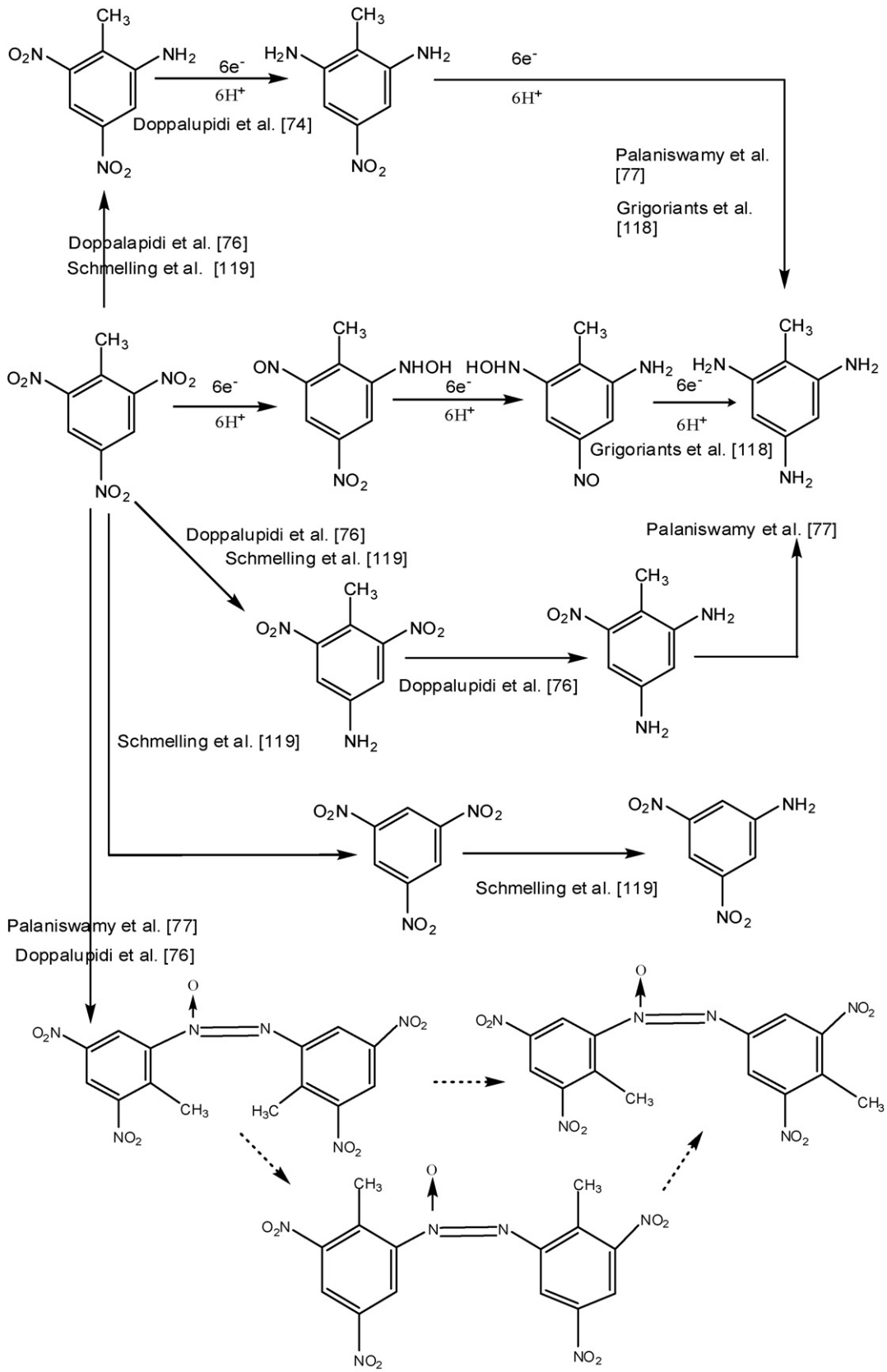

Fig. 8. Proposed mechanisms for TNT transformation under electrochemical reduction process.

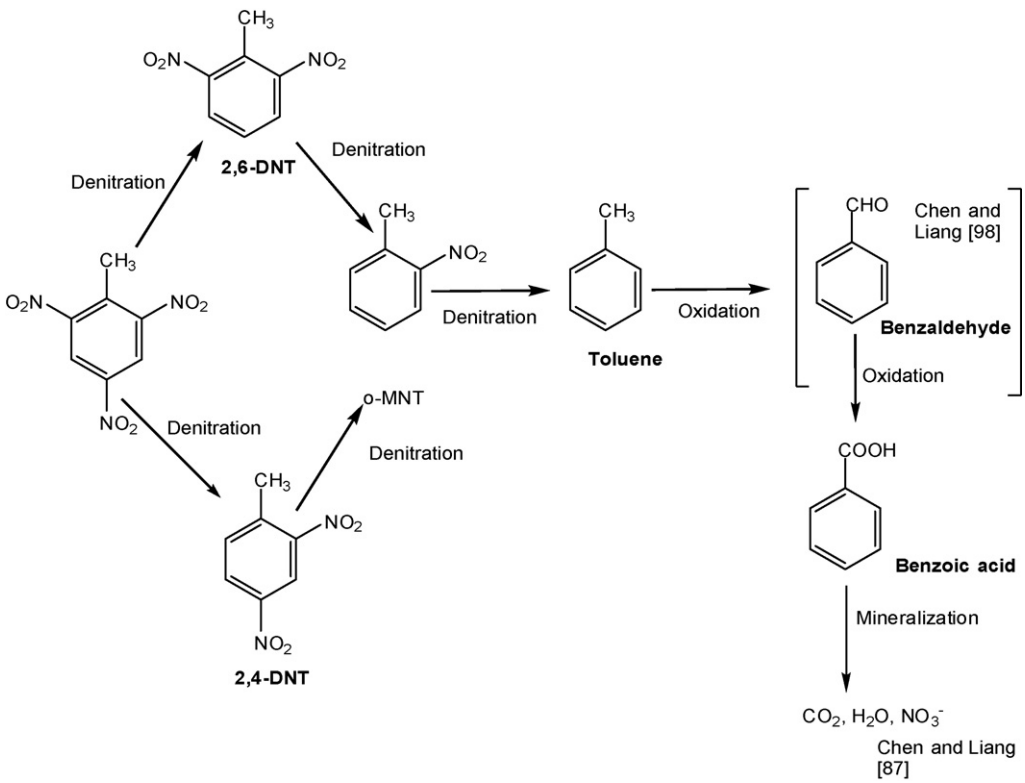

Fig. 9. Plausible reaction pathways for TNT oxidation in spent acid by electro-Fenton treatment.

4-hydroxylamino-2,6-dinitrotoluene, 2,4,6-triaminotoluene, 2,2′,6,6′-tetranitro-4,4′-azoxytoluene 4,2′,6,6′-tetranitro-2,4′-azoxytoluene and 2,2′,4,4′-tetranitro-6,6′-azoxytoluene and triaminotoluene). In both cases there is a reduction, but it seems that the mix proportions and the masses percentage of identified products differ.

Looking closely at the degradation products and mechanisms generated, it is surprising to find that Chen et al. [39,72] reproduced the same by-products and the same pattern of mineralization of TNT and 2,4-DNT under two different processes: UV/O_3 and Fenton. The same authors have also reproduced the same reaction pathways by electrochemical oxidation and electro-Fenton treatment in spent acid Chen and Liang [89,100]. We can attribute this similarity to the use of the same analytical tool which is the (GC/MS) in this case and may not be accurate to identify correctly the by-products formed.

It is important to note that during this bibliographic search, we did not found any work related to the study of toxic by-products of TNT produced by advanced oxidation processes. Considering a possible coupling between these processes and the biodegradation reduces the cost of chemical reagents and energy. Unfortunately, this route has not been well explored and further research should be done in this direction.

However, Schrader and Hess [101] have studied the coupled abiotic–biotic to Fenton modified reaction for TNT mineralization and demonstrated that 100% degradation could be obtained under each reaction condition (Fe^{3+}, H_2O_2, acidic and neutral pH in modified and dark Fenton). Using this coupled reaction process, abiotic, dark-Fenton reaction), TNT mineralization at pH 3 was increased from 47 to 80% using a microbial biomass. Likewise, Kröger et al. [102] and Kröger and Fels [103] have studied the possibility of a combining biological–chemical process. However, in contrast to the studies starting with a chemical treatment, these authors presented the concept of a biological reduction of TNT prior to an oxidative chemical treatment by advanced oxidation process (photo-Fenton), which seems to be the most appropriate approach towards mineralization of TNT (unfortunately, no data regarding TOC or COD were available).

6. Conclusions

This review constitutes a reference document in the field of TNT removal by advanced oxidation processes and will help the researchers to launch new technological devices and applications as well as promoting TNT degradation.

Fenton-based reactions are capable of extensively degrading TNT in a variety of aqueous solutions. Rigorous economic comparisons using an accepted standard measure of treatment efficiency are scarce. However, Fenton reactions can be performed at ambient temperature and do not require illumination, although they are usually enhanced by it. The reagents are readily available, easy to store, relatively safe to handle, and non-threatening to the environment. Biological wastewater treatment may be improved with the addition of a Fenton pre-treatment step. Drawbacks associated with the use of Fenton oxidation are the need to firstly reduce the pH, followed by a subsequent neutralisation. These drawbacks are intrinsic; others may be alleviated after further research and development. In addition, Fenton AOPs suffer from the same disadvantages that other hydroxyl radical-AOPs do: namely, they are susceptible to scavenging of hydroxyl radicals by non target substances (e.g., natural organic matter, halides), and are unsuitable for certain compounds (such as perchlorinated compounds) that resist attack by hydroxyl radicals. On the other hand more efforts are required to establish conclusively whether Fenton's reagent can be used efficiently for the treatment of complex real effluents especially in the presence of large amount of ionic species. Studies are required in this direction in terms of experimentation and development of kinetic models.

Overall it can be said that Fenton oxidation, by far, appears to be the best technology whereas photocatalytic appears to be little

less efficient for TNT removal. Efforts are indeed required both on experimental front as well as kinetic modelling before application on large-scale is feasible with high degree of efficiency and lower treatment costs.

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